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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objective of this program was to bring together four investigators whose expertise was in the area of polymer synthesis, characterization, rheology and processing, solid state morphology and mechanical behavior, and to integrate these efforts toward the synthesis of new elastomers and polymeric matrix resins suitable for organic composites. The abstract describes some highlights of research findings and potential applications. In addition, in an appendix we have included statistics on publications, preprints, and MS and PhD theses supported by this contract.			
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Liquid crystalline copolymers are of great current interest and have already been demonstrated to be important reinforcing fibers for both elastomers and composites. This study has principally dwelt upon the relationships between chemical structure, rheology, morphology, and mechanical behavior. In addition, thermotropic polyesters and their blends with conventional PET have also been examined and show promise as advanced materials.

Inverse gas chromatography (IGC) has been used to probe polymer coatings with a variety of organic liquids as the mobile phase. Depending upon the relative retention times, important thermodynamic behavior can be derived. This has applications in the swelling of polymers and elastomers and also in the transport of agents through solid polymeric films. A second important technique that has been studied and further developed by this research is solid state NMR. This method has the ability to identify and define chemical structure and possibly molecular motion in elastomers, glasses, and various network structures.

Polyisobutylene ion containing copolymers containing sulfonate end groups were investigated. Trifunctionality allowed for excellent mechanical properties as a combined result of ionic associations and strain induced crystallization. The ionic reinforcing phase could lead to new elastomeric materials with interesting transport properties that could possibly catalyze the decomposition of liquid agents.

The synthesis efforts over the three-year ARO research contract were extensive and focused on anionic, cationic, ring-opening, and group transfer synthetic methods for the preparation of novel homo- and block copolymer elastomers based upon hydrogenated dienes, methacrylates, epoxides, and siloxanes. The numerous publications based upon this work are included in the appendix section A. Suffice it to say that a number of novel materials were generated, several of which showed important new physical properties. In addition to the focus on elastomeric materials, the second area of intense interest was the development of new and modified matrix materials. In this latter area, effort was extended to further understand the fundamentals of poly(arylene ether)s, including the first demonstration of molecular motion in deuterium labeled poly(arylene ether)s using deuterium NMR measurements. The results indicated that the arylene ether bonds underwent 180° ring flips even at temperatures, e.g. well below the glass transition temperature. Additional efforts were focused on the modification of engineering polymers with thermally stable siloxane systems. Emphasis was placed on further studies of the bulk and solution phase separation characteristics of these new materials and it was clearly demonstrated that selective surface migration of the hydrophobic siloxane chains could occur. This phenomena is no doubt important in membrane technology, as well as in biomaterials.

ELASTOMERS AND OTHER ORGANIC COMPOSITES

FINAL REPORT

J. E. MCGRATH, G. L. WILKES, D. G. BAIRD, T. C. WARD

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APPENDIX

(A) Publications:

1. J. E. McGrath, Editor, "Ring Opening Polymerization: Kinetics, Mechanisms and Synthesis," ACS Symposium Series, No. 286 (1985).
2. E. Yorkgitis, C. Tran, N. Eiss, I. Yilgor, G. L. Wilkes and J. E. McGrath, "Siloxane Modifiers for Epoxy Resins," Adv. in Chem., No. 208, 137-163 (1984).
3. E. Yorkgitis, C. Tran, N. Eiss, G. L. Wilkes and J. E. McGrath, "A Review of Siloxane Modified Epoxy Networks," Advances in Polym. Sci., No. 72, 79-109 (1985).
4. R. D. Allen, I. Yilgor and J. E. McGrath, "Synthesis of Ion Containing Polymers," in "Ion Containing Polymers," A. Eisenberg, Ed. (1985).
5. R. D. Allen, T. E. Long and J. E. McGrath, "Synthesis of Tactic Poly(Alkyl Methacrylate) Homo- and Copolymers," in "Advances in Polymer Synthesis," J. E. McGrath and B. M. Culbertson, Eds., Vol. 31, 347-362, Plenum Press, New York (1985).
6. T. E. Long, R. D. Allen, and J. E. McGrath, "Controlled Synthesis of Various Poly(Alkyl Methacrylates) by Anionic Techniques," in Recent Advances in Mechanistic and Synthetic Aspects of Polymerization, Series C Vol. 215, Chap. 2, p.79, M. Fontanille and A. Guyot, Editors, D. Reidel Publishing Company (1987).
7. T. E. Long, R. D. Allen and J. E. McGrath, "Synthesis and Characterization of Block Copolymers Containing Acid and Ionomeric Functionalities," in Chemical Reactions in Polymers, J. L. Benham and J. F. Kinstle, Eds., ACS Symposium Series No. 364, Chap. 19, p. 258 (1988).
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12. D. Tyagi, I. Yilgor, J. E. McGrath and G. L. Wilkes, "Segmented Organosiloxane Copolymers. II. Thermal and Mechanical Properties of Siloxane Urea Copolymers," *Polymer*, London, 25(12), 1807-1814 (1984).
13. I. Yilgor, J. Riffle and J. E. McGrath, "Reactive Difunctional Siloxane Oligomers: Synthesis and Characterization," *Reactive Oligomers*, ACS Symposium Series, No. 282, 161-174 (1985).
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19. D. Tyagi, J. L. Hedrick, D. C. Webster, J. E. McGrath and G. L. Wilkes, "Structure-Property Relationships in Perfectly Alternating Segmented Polysulfone/Polydimethylsiloxane Copolymers," *Polymer*, 29, pp. 833-844 (1988).
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23. D. R. Lloyd, T. C. Ward, and H. P. Schreiber, Eds., "Inverse Gas Chromatography," *ACS Symp. Series No. 391* (1989).
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28. M. R. Tant, J. H. Song, G. L. Wilkes, J. Horron, and R. Jerome, *Polymer*, 27, 1815-1818 (November, 1986).
29. Eugene Joseph, Garth L. Wilkes, and D. G. Baird, *Polymer*, 26, 689-703 (May, 1985).
30. Richard C. Allen, Garth L. Wilkes, Iskinde Yilgor, Dshilian Wu, and James E. McGrath, *Makromol. Chem.*, 187, 2909-2931 (1986).
31. A. D. Gotsis and D. G. Baird, *Rheologica Acta*, 25, 275-286 (1986).
32. D. Done and D. G. Baird, *Poly. Eng. Sci.*, 27(11), 816-822 (June, 1987).
33. Kent G. Blizzard and Donald G. Baird, *Polym. Eng. Sci.*, 27(9), 653-662 (May, 1987)

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1. R. D. Allen and J. E. McGrath, "Synthesis of Tactic Poly(Alkyl Methacrylate) Homo- and Copolymers," *Polymer Preprints*, 25(2), 9-11 (1984).
2. J. L. Hedrick, R. A. Patsiga and J. E. McGrath, "Synthesis and Characterization of Deuterated Poly(Arylene Ether Sulfones)," *Polymer Preprints*, 25(2), 88-90 (1984).
3. P. K. Das, J. M. Hoover, R. J. Dodson, T. C. Ward and J. E. McGrath, "Study of Dilute Solution Properties of Polystyrene (and Substituted Styrene)-b-Polybutadiene Diblock Copolymers by Variable Temperature Size Exclusion Chromatography," *Polymer Preprints*, 25(2), 96-97 (1984).
4. M. M. Sheridan, J. M. Hoover, T. C. Ward and J. E. McGrath, "Viscoelastic Properties of Radial Substituted Styrene-Isoprene Block Copolymers," *Polymer Preprints*, 25(2), 102-104 (1984).
5. M. M. Sheridan, J. M. Hoover, T. C. Ward and J. E. McGrath, "Role of Microphase Separation in Adhesion," *Polymer Preprints*, 26(1), 186-188 (1985).
6. P. Koning, T. C. Ward, R. D. Allen and J. E. McGrath, "Thermodynamics of Acid-Base Polymer/Solute Interactions via Inverse Gas Chromatography," *Polymer Preprints*, 26(1), 189-190 (1985).

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14. T. E. Long, C. D. DePorter, N. Patel, D. W. Dwight, G. L. Wilkes and J. E. McGrath, "Poly(Alkyl Methacrylate-Methacrylate Carboxylate) Ion-Containing Block Copolymers," ACS National Meeting, New Orleans, LA, Polymer Preprints, 28(2), 214-216 (1987).
15. S. D. Smith, J. M. DeSimone, G. York, D. W. Dwight, G. L. Wilkes and J. E. McGrath, "Blends of Poly(Methyl Methacrylate)-Poly(Dimethyl Siloxane) Graft Copolymers with Poly(Methyl Methacrylate) and Poly(Vinyl Chloride)," ACS National Meeting, New Orleans, LA, Polymer Preprints, 28(2), 150-152 (1987).
16. P. A. Wood, D. Bradley, J. M. Hoover, M. K. Martin, D. Chen, S. Kilic, T. C. Ward, and J. E. McGrath, "Synthesis and Hydrogenation of Linear and Star Block Copolymers Based on Butadiene - Isoprene - Divinylbenzene," ACS National Meeting, Toronto, Canada, Polymer Preprints, 29(1), 366-368 (1988).
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19. A. M. Hellstern, J. M. DeSimone and J. E. McGrath, "Fundamental Investigations of the Group Transfer Polymerization of Various Alkyl Methacrylates Using Tetrabutyl Ammonium Benzoate as the Catalyst," ACS National Meeting, Los Angeles, CA, Polymer Preprints, 29(2), 342-344 (1988).
20. J. E. McGrath, A. M. Hellstern, J. M. DeSimone, T. E. Long, C. Cho, Y. Yoo, P. Wood, C. D. DePorter, and J. S. Riffle, "Advances in Heterophase Copolymer Synthesis," ACS National Meeting, Los Angeles, CA, Polymer Preprints, 29(2), 57-60 (1988).
21. C. D. DePorter, L. N. Venkateshwaran, G. A. York, G. L. Wilkes, and J. E. McGrath, "Synthesis and Characterization of Well Defined Acrylic Ion-Containing Di- and Triblock Copolymers," ACS National Meeting, Dallas, TX, Polymer Preprints, 30(1), 201-203 (1989).

(C) Theses (since 1984); ARO Support:

1. R. D. Allen, Ph.D., Chemistry, June 1985, "Synthesis of Novel Methacrylate-Containing Polymers by Anionic Polymerization." Current Employer: IBM; San Jose, California.
2. P. Sormani, Ph.D., Chemistry, February 1986, "The Ring-Opening Polymerization of Cyclosiloxanes in the Presence of Bis(α , ω -aminopropyl)-1-3-Tetramethyldisiloxane." Current Employer: DuPont; Wilmington, Delaware.
3. J. Senger, M.S., Chemistry, November 1986, "Polyhydroxy Ethers, Synthesis, Analysis, and Crosslinking," Ph.D. Candidate, Materials Engineering Science.
4. S. D. Wu, Ph.D., Chemistry, June 1987, "Synthesis and Characterization of Modified Poly(Arylene Ether Ether Ketone) Copolymers." Current Employer: EniMont; Monmouth Junction, New Jersey.
5. S. D. Smith, Ph.D., Chemistry, August 1987, "Synthesis of Novel Siloxane-Containing Block and Graft Copolymers by Anionic Polymerization and Macromonomer Technique." Current Employer: Procter & Gamble; Cincinnati, Ohio.
6. T. E. Long, Ph.D., Chemistry, October 1987, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems." Current Employer: Eastman Kodak; Rochester, New York.

7. J. A. Cecere, Ph.D., Materials Engineering Science, February 1988, "Structure-Property Relationships of Functionalized Modifiers for Thermosetting Resin Systems."
Current Employer: Brunswick Corporation; Marion, Virginia.
8. C. Cho, Ph.D., Chemistry, March 1988, "Controlled Polymerization of Vinyl Alkyl Ethers."
Current Employer: DuPont; Wilmington, Delaware.
9. A. Hellstern, Ph.D., Chemistry, February 1989, "Synthesis, Characterization, and Kinetic Investigation of Heterophase Materials Prepared Using Group Transfer Polymerization,"
Current Employer: GE, Schenectady, New York.
10. R. Kim Yoon, M.S. Graduate, Materials Engineering, December 1989, "Siloxane Modified Polyurea and Polyurethane Urea Segmented Copolymers".
11. P. Wood, M.S., Chemistry, September 1988, "Synthesis and Characterization of Linear and Star-Branched Butadiene-Isoprene Block Copolymers and Their Hydrogenated Derivatives,"
Ph.D Candidate, Chemistry.
12. C. DePorter, Ph.D. Candidate, Chemistry.
13. N. M. Patel, Ph.D. Candidate, Materials Engineering Science.
14. G. A. York, Ph.D. Candidate, Materials Engineering Science.
15. Dr. S. Kilic, Visiting Scientist, University of Ankara, 1985-June 1988
Current Employer: PPG, Pittsburgh, PA
16. Dr. D. K. Mohanty, June 1983-September 1983
February 1985-August 1988
Current Employer: Dept. of Chemistry, Central Michigan University
(Assistant Professor)
17. Margaret Sheridan, PhD, 1986;
Current Employer: 3M.
18. Ed Balcells, MS, Medical School.
19. Paul Koning, PhD, 1988;
Current Employer: Amoco Chemical.
20. Dr. Liao Kairong, China.
21. Ken G. Blizzard, MS, February 1986; PhD, March 1988.
22. Dishong S. Done, PhD, June 1987.
23. S. Bagrodia, PhD, 1985;
Current Employer: Eastman Kodak.

24. R. Pisipati, PhD, 1986;
Current Employer: Mobay, Bayer, USA.

25. M. R. Tant, PhD, 1986;
Current Employer: Eastman Kodak

26. Eugene Joseph, PhD, 1987;
Current Employer: 3M.

27. Richard C. Allen, PhD, 1985;
Current Employer: 3M

28. A. D. Gotsis, PhD, 1985.